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UNIVERSAL SELF-DIFFUSION COEFFICIENTS OF MACROMOLECULES IN POLYMER SOLUTIONS AND MELTS AS A FUNCTION OF CONCENTRATION AND MOLECULAR MASS*

V. D. SKIRDA, V. I. SUNDUKOV, A. I. MAKLAKOV and G. I. VASIL'EV

V. I. Lenin State University, Kazan

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On the basis of an analysis of experimentally determined coefficients of self-diffusion D_s for polystyrene, polyethylene oxide (PEO), polydimethylsiloxane, and dextran in different solvents over a wide range of MM variation and concentrations φ, it is shown that there are universal relations between D_s and between D_s and M.

THE DEVELOPMENT of theories based on the concept of scaling [1] and reptation [2] motion mechanisms is one of the factors resulting in accelerated experimental study of macromolecule self-diffusion in polymer systems. However, in spite of the considerable accumulation of experimental data such fundamental problems as the coefficients of self-diffusion D_s of polymer chains as a function of concentration and MM remain purely at the discussion level. In particular, the discussion of D_s as a function of concentration lies mainly within the framework of a search for the asymptotic scaling laws predicted by theory.

In the case of the relation between D_s and MM, in most papers [3, 4] it is noted that there are no special features in the region of critical M values. Consequently, the relation between D_s and M is discussed independently of the relation between D_s and concentration.

The object of this work was to find general laws for the plots of D_s against M and φ based on the analysis of experimental results obtained with different polymers over a wide range of variation of the polymer bulk concentrations and MM, and also using a relatively wide selection of solvents. The starting point for the argument is the assumption that the plots of D_s against φ obey [5] the universal function $f(\varphi/\hat{\varphi})$ of the dimensionless parameter $\varphi/\hat{\varphi}$, where $\hat{\varphi}$ is a certain critical concentration, which depends, in particular, on the polymer MM.

A NMR method [6] with a pulsed gradient magnetic field was used to study the self-diffusion of the PEO macromolecules, marketed by the firm "Fluka-Buchs" of number average MM $M_n = (2\times10^{-3})$–(4×10^4) ($M_w/M_n \lesssim 1{\cdot}1$) and $M_n = 3\times10^6$ ($M_w/M_n \sim 2$), manufactured by Union Carbide, in dioxane, chloroform, dibutyl phthalate, acetonitrile, and benzene; the PS "Standard"

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